TRANSLATION

I, YukoMitsui, residing at 4-6-10, Higashikoigakubo, Kokubunji-shi, Tokyo, Japan, state:

that I know well both the Japanese and English languages,

that I translated, from Japanese into English, Japanese Patent Application No. 2003-016659, filed on January 24, 2003, and

that the attached English translation is a true and accurate translation to the best of my knowledge and belief.

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[Document] SPECIFICATION

[Title of the Invention] FILM-FORMATION METHOD

[What is Claimed is:]

[Claim 1] A film-formation method of supplying a process gas into a process container which can be evacuated, and forming a silicon nitride film on a target substrate at a predetermined process temperature, the method characterized in that

the process gas includes ammonia gas and hexaethylamino-disilane.

[Claim 2] The method according to claim 1, characterized in that the process temperature is set to be within a range of from 430 to 550°C.

[Claim 3] The method according to claim 1 or 2, characterized in that a flow rate of the ammonia gas is set to be within a range of from 30 to 90 times as high as a flow rate of the hexaethylaminodisilane gas.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a film-formation method of forming a silicon nitride film (SiN).

[0002]

[Prior Art]

In general, semiconductor devices include insulating films made of a material, such as SiO_2, PSG (Phospho Silicate Glass), P(plasma)-SiO, P(plasma)-SiN, SOG (Spin On Glass), Si_3N_4 (silicon nitride film), etc.

Conventionally known is a method of forming a silicon oxide film or silicon nitride film on the surface of a semiconductor wafer by thermal CVD (Chemical Vapor Deposition). In such thermal CVD, a silane family gas, such as monosilane (SiH_4), dichlorosilane (SiH_2Cl_2), hexachlorodisilane (Si_2Cl_6), or bistertialbutylamino-silane (BTBAS), is used as a film-forming gas (see, for example, Pat. Document 1).

Specifically, for example, where a silicon oxide film is deposited, such a gas combination is used, as SiH_4 + N_2O, SiH_2Cl_2 + N_2O, or TEOS (tetraethyl-orthosilicate) + O_2, thereby forming a silicon oxide film by thermal CVD (Chemical Vapor Deposition). Where a silicon nitride film is deposited, such a gas combination is used, as SiH_2Cl_2 + NH_3, or Si_2Cl_6 + NH_3, thereby forming a silicon nitride film by thermal CVD.

[0003]

Meanwhile, with increased miniaturization and integration of semiconductor integrated circuits, insulating films need to be thinner than those aforementioned. Furthermore, in order to maintain the electric properties of the various films that lie below insulating films, the temperature used in thermal CVD in forming the insulating films needs to be lowered.

In this respect, for example, where a silicon nitride film is deposited by thermal CVD, a high process temperature of about 760°C is conventionally used. In recent years, where a silicon nitride film is deposited by thermal CVD, a process temperature of about 600°C is used, as the case may be. In addition, as is commonly known, where a semiconductor

integrated circuit is formed, electrical conducting layers and aforementioned insulating layers are deposited one on top the other while pattern etching is being conducted at the same time, thus constructing a multi-layered structure.

[0004]

[Pat. Document 1]

Jpn. Pat. Appln. KOKAI Publication No. 11-172439

[0005]

[Object of the Invention]

After such an insulating film as described above is formed, contaminants such as organic substances and particles may be stuck to the surface of the insulating film. In order to remove the contaminants, a cleaning process is performed, before another thin film is formed on the insulating film. In this cleaning process, the semiconductor wafer is immersed in a cleaning solution, such as dilute hydrofluoric acid, and the surface of the insulating film is etched by a very small amount, thereby removing the contaminants.

Where the insulating film is formed by thermal CVD at a higher process temperature of, e.g., about 760°C, the etching rate of the insulating film during the cleaning process is very small. Accordingly, the insulating film is not excessively etched by cleaning, and thus the cleaning process is performed with high controllability in the film thickness.

[0006]

On the other hand, where the insulating film is formed by thermal CVD at a lower process temperature of, e.g., about 600°C, the etching rate of the insulating film during the

cleaning process is relatively large. Accordingly, the insulating film may be excessively etched by cleaning, and thus the cleaning process entails lower controllability in the film thickness.

The present invention has been achieved by focusing attention on the problems described above, which are to be efficaciously solved. An object of the present invention is to provide a film-formation method by which the etching rate of a film during a cleaning process can be made relatively small even if the film is formed at a relatively low temperature, and thus the cleaning process is performed with high controllability in the film thickness.

[0007]

[Means for Achieving the Object]

The present inventors intensively studied the etching rate of an insulating film during a cleaning process, and arrived at the findings: the etching rate of an insulating film during a cleaning process can be reduced by using hexaethylamino-disilane.

According to the invention described in claim 1, there is provided a film-formation method of supplying a process gas into a process container which can be evacuated, and forming a silicon nitride film on a target substrate at a predetermined process temperature, the method characterized in that the process gas includes ammonia gas and hexaethylamino-disilane gas.

With this method, ammonia gas and hexaethylamino-disilane gas are used as process gases to form a silicon nitride film.

Therefore, the etching rate of the silicon nitride film during the cleaning process can be made relatively small, and thus, the cleaning process can be performed with high controllability in the film thickness.

[0008]

In this case, for example, as defined in claim 2, the process temperature is set to be within a range of from 430 to 550°C.

Further, for example, as defined in claim 3, a flow rate of the ammonia gas is set to be within a range of from 30 to 90 times higher than a flow rate of the hexaethylaminodisilane gas.

[0009]

[Embodiment]

Now an embodiment of a film-formation method according to the present invention will be described in detail in accordance with the appended drawings.

FIG. 1 is a view showing the configuration of a film-formation apparatus used for carrying out the method of the invention.

The film-formation apparatus 2 is arranged to supply a process gas including hexaethylaminodisilane [$C_{12}H_{36}N_6Si_2$] (which will be referred to as HEAD, as well) gas used as a silicon-containing material gas, and NH_3 gas, so as to deposit a silicon nitride film (which will be referred to as SiN, as well). The film-formation apparatus 2 includes a process container 8 having a double tube structure, formed of an inner tube 4 and an outer tube 6, the both of which are formed of

cylindrical quartz bodies, and disposed concentrically with each other with a predetermined gap 10 therebetween. The process container 8 is surrounded by a heating cover 16, which includes a heating means 12, such as an electrical heater, and a thermal insulator 14. The heating means 12 is disposed over the entire inner surface of the thermal insulator 14.

[0010]

The bottom of the process container 8 is supported by a cylindrical manifold 18 made of, e.g., stainless steel. A ring support plate 18A extends inward from the inner wall of the manifold 18 and supports the bottom of the inner tube 4. A wafer boat 20 made of quartz and serving as a target substrate holding means loads a pile of semiconductor wafers W as multiple target substrates, and is moved up and down through the bottom port of the manifold 18, so that the wafer boat 20 is loaded/unloaded into and from the process container 8. In this embodiment, for example, the wafer boat 20 can support 150 product wafers having a diameter of 200 mm and 20 dummy wafers at essentially regular intervals in the vertical direction. In other words, the wafer boat 20 can accommodate 170 wafers in total.

[0011]

The wafer boat 20 is placed on a rotary table 24 through a heat-insulating cylinder 22 made of quartz. The rotary table 24 is supported by a rotary shaft 28, which penetrates a lid 26 used for opening/closing the bottom port of the manifold 18.

The portion of the lid 26 where the rotary shaft 28

penetrates is provided with, e.g., a magnetic-fluid seal 30, so that the rotary shaft 28 is rotatably supported in an airtightly sealed state. A seal member 32, such as an O-ring, is interposed between the periphery of the lid 26 and the bottom of the manifold 18, so that the interior of the process container can be kept sealed.

[0012]

The rotary shaft 28 above described is attached at the distal end of an arm 36 supported by an elevating mechanism 34, such as a boat elevator. The elevating mechanism 34 moves the wafer boat 20 and lid 26 up and down integratedly. An exhaust port 38 is formed in the side of the manifold 18 to exhaust the atmosphere in the process container through the bottom of the gap 10 between the inner tube 4 and outer tube 6. The exhaust port 38 is connected to a vacuum exhaust section (not shown) including a vacuum pump and so forth.

A gas supply means 40 is connected to the side of the manifold 18 to supply predetermined process gases into the inner tube 4. More specifically, the gas supply means 40 includes a film-forming gas supply circuit 42 and a nitriding gas supply circuit 44. The gas supply systems 40 and 42 respectively include linear film-forming gas nozzle 48 and nitriding gas nozzle 50, which penetrate the sidewall of the manifold 18.

[0013]

The gas nozzles 48 and 50 are respectively connected to a film-forming gas passage 60 and a nitriding gas passage 62, which are respectively provided with flow rate controllers 54

and 56, such as mass-flow controllers, so as to respectively supply the film-forming gas and nitriding gas at controlled flow rates. In this embodiment, for example, the film-forming gas is HEAD, and the nitriding gas is NH_3 gas. The inner tube 4 of the process container 8 has an inner diameter of about 240 mm, and a height of about 1300 mm. The process container 8 has a volume of about 110 liters.

[0014]

Next, an explanation will be given of a film-formation method according to the present invention, performed in the apparatus described above.

At first, when the film-formation apparatus is in a waiting state with no wafer boat loaded therein, the interior of the process container 8 is kept at a process temperature of, e.g., about 450°C. The wafer boat 20 at a normal temperature and loading a number of wafers, e.g. 150 product wafers W and 20 dummy wafers, is loaded into the process container 8 from below, by moving up the lid 26. Then, the bottom port of the manifold 18 is closed by the lid 26 to airtightly seal the interior of the process container 8.

Then, the interior of the process container 8 is vacuum exhausted to a predetermined process pressure of, e.g., about 106 Pa (0.8 Torr). Also, the wafer temperature is increased to a process temperature for film-formation of, e.g., about 450°C. At this time, the apparatus is in a waiting state until the temperature becomes stable. Then, predetermined process gases including HEAD gas and the nitriding process gas including NH_3 gas are supplied from the respective nozzles 48

and 50 of the gas supply means 40 at controlled flow rates. The two process gases are supplied into the bottom portion of the process container 8 and mixed there. Then, the gases react with each other while flowing upward in the process space S, and cause a silicon nitride thin film to be deposited on the surface of each wafer W.

[0015]

The process gases thus flowing upward in the process space S bounce off the ceiling of the process container 8, and flow through the gap 10 between the inner tube 4 and outer tube 6, and then are exhausted through the exhaust port 38 out of the process container 8. In this film-formation, the process temperature is preferably set to be within a range of from 430 to 550°C. The NH_3 gas flow rate is preferably set to be within a range of from 30 to 90 times as high as the HEAD gas flow rate. The NH_3 gas flow rate is preferably set to be within a range of from 10 to 30 sccm. The process pressure is preferably set to be within a range of from 27 Pa to 1333 Pa (0.2 to 10 Torr).

[0016]

In this manner, if a silicon nitride film is formed on the surface of each wafer by thermal CVD using NH_3 gas and HEAD gas, the silicon nitride thus formed brings about a low etching rate relative to dilute hydrofluoric acid used in a cleaning process on the surface of the silicon nitride film despite of that the film formation is performed at a temperature of about 760°C or lower, which is a process temperature for a conventional film-formation method performed

using, for example, dichlorosilane and NH_3 gas. As a consequence, the silicon nitride film can be prevented from being excessively etched during the cleaning process, thereby improving the controllability in the film thickness.

[0017]

A silicon nitride film was formed under different process conditions, such as the process temperature, gas flow rate (gas flow rate ratio), and process pressure, and then the etching rate of the film was measured. The measurement result will be explained below.

FIG. 2 is a graph showing the relationship between silicon nitride films deposited under different process conditions and their etching rates. Here, for the purpose of comparison, a measurement result as for a silicon nitride film (partly using ethylene gas) formed using hexa-chlorodisilane (which will be referred to as HCD, as well) is given.

In FIG. 2, the etching rates are shown as normalized etching rates, which are ratios relative to a reference value "1" (see, characteristic A), the reference value (characteristic A) being the etching rate of a silicon nitride film, which was formed by a method (conventional film-formation method) using ammonia gas and dichlorosilane (DCS) at a process temperature of about 760°C.

[0018]

The characteristic B in FIG. 2 corresponds to a film-formation process using HCD and NH_3 at a process temperature of 600°C. In this case, the normalized etching rate of an SiN film increased to 5.01, due to the temperature lower by about

160°C than that of the characteristic A, in addition to the gas difference. This result is unfavorable.

The characteristic C corresponds to a film-formation process using HCD and NH_3 (with ethylene gas partly added thereto) at a process temperature of 450°C. In this case, the normalized etching rate of an SiN film increased to 21.75, due to the temperature further lower by about 150°C than that of the characteristic B, and the film quality is extremely deteriorated. This result is very unfavorable.

On the other hand, the characteristic D in FIG. 2 corresponds to a film-formation process using HEAD and NH_3 at a process temperature of 550°C. In this case, the normalized etching rate of an SiN film became about 0.10. This result is very favorable, because the etching rate is as small as 1/10 of the characteristic A.

[0019]

The characteristics E and F in FIG. 2 correspond to film-formation processes using HEAD and NH_3 at lower process temperatures of 450°C and 430°C, respectively. In these cases, the normalized etching rates of an SiN film became about 0.67 and 1.44, respectively. The characteristics E and F are not so good, as compared to the characteristic D, but they are close to the characteristic A. Accordingly, the characteristics E and F are favorable.

Furthermore, a film-formation process was performed, using HEAD and NH_3 at a process temperature of 400°C. The film formed by this process consisted essentially of SiO_2, i.e., no SiN film was formed.

[0020]

It has been found from the results described above that, even where a lower process temperature of from 430 to 550°C is used, as shown in characteristics D to F, a formed SiN film can have an etching rate almost the same as or still lower than that of an SiN film formed by a conventional process using DCS gas at a process temperature of 760°C.

Furthermore, the quality of the SiN film of the characteristics D to F was analyzed. The SiN film of the characteristic F was somewhat lower in quality than the SiN films of the characteristics D and E, in terms of the doped nitrogen amount.

Accordingly, it has been found that the process temperature is preferably set to be within a range of from 450 to 550°C, in light of the quality of an SiN film as well.

[0021]

In the characteristics D to F, the gas flow rate of HEAD gas was set at different values within a range of from 10 sccm to 30 sccm, while the gas flow rate of NH_3 gas was set at a constant value of 900 sccm. In other words, the ratio of the flow rate of NH_3 gas relative to that of HEAD gas was changed within a range of from 30 to 90 times. In these cases, however, each of the formed SiN films had a small etching rate and good film quality.

As shown in the characteristics D to F, the process pressure was set at different values within a range of from 27 Pa (0.2 Torr) to 106 Pa (0.8 Torr), in which the formed SiN films had good film quality. Furthermore, additional

experiments were performed while increasing the process pressure up to 1330 Pa (10 Torr). Also in this case, each of the formed SiN films had a small etching rate and good film quality.

[0022]

In the above embodiment, the film-formation apparatus is a vertical film-formation apparatus of the batch type. The present invention is not limited to this, and it may be applied to a horizontal film-formation apparatus of the batch type, or a film-formation apparatus of the single-substrate type arranged to process target substrates one by one.

As regards a target substrate, other than a semiconductor wafer, the present invention may also be applied to a glass substrate or LCD substrate.

[0023]

[Advantage of the Invention]

As described above, according to the film-formation method of the present invention, a sufficient functional effect as below can be exhibited.

Because ammonia gas and hexaethylamino-disilane gas are used to form a silicon nitride film, the etching rate of the silicon nitride film during a cleaning process can be made relatively small, and thus, the cleaning process can be performed with high controllability in the film thickness.

[Brief Description of the Drawings]

[FIG. 1]

A view showing the configuration of a film-formation apparatus used for carrying out the method according to the

present invention.

[FIG. 2]

A graph showing the relationship between silicon nitride films deposited under different process conditions and their etching rates.

[Explanation of Reference Symbols]

2: Film-formation apparatus

8: Process Chamber

12: Heating means

20: Wafer boat (target substrate supporting means)

40: Gas supply means

42: Film-forming gas supply circuit

44: Nitriding gas supply circuit

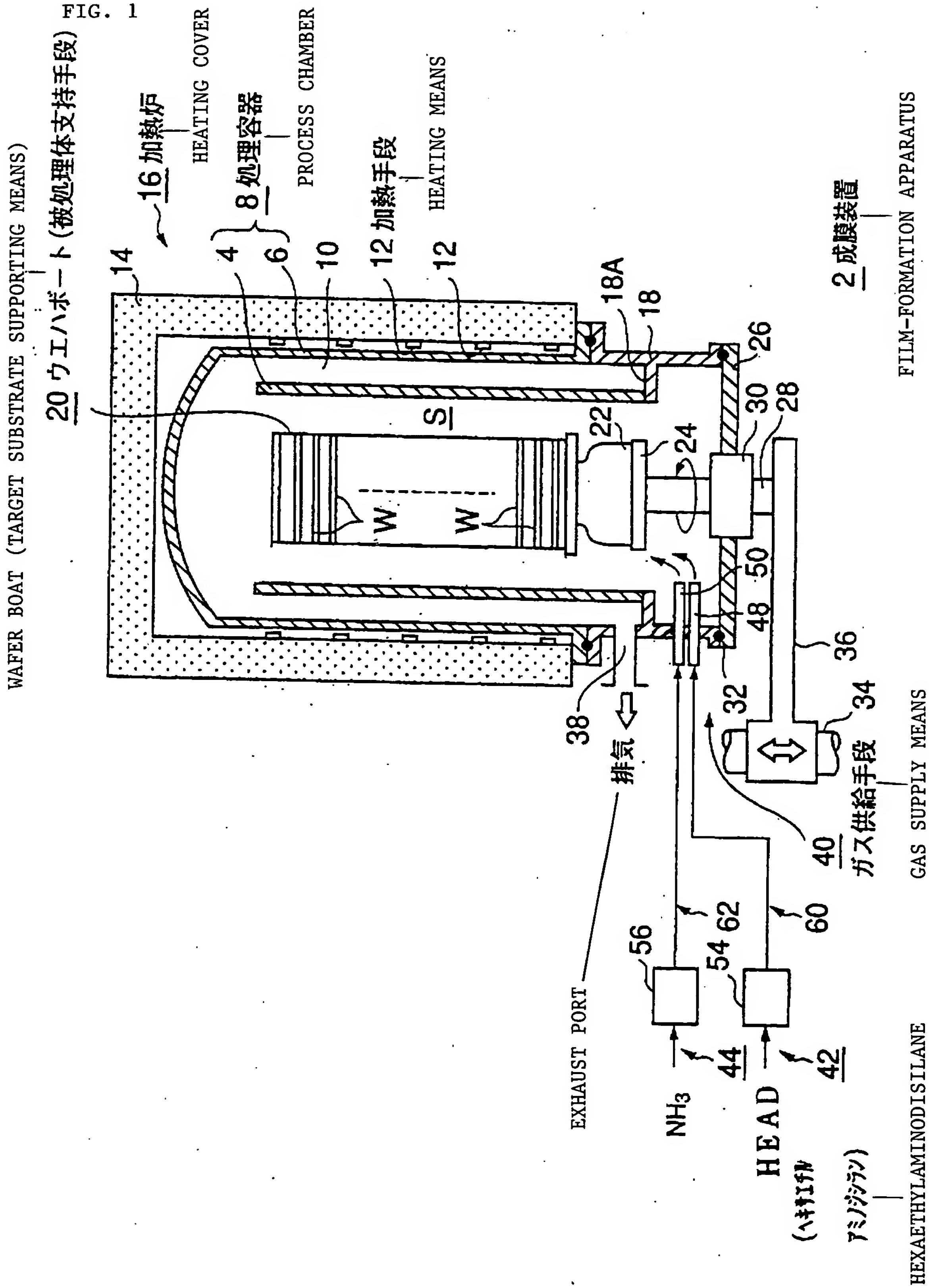
60: Film-forming gas passage

62: Nitriding gas passage

W: Semiconductor wafer (target substrate)

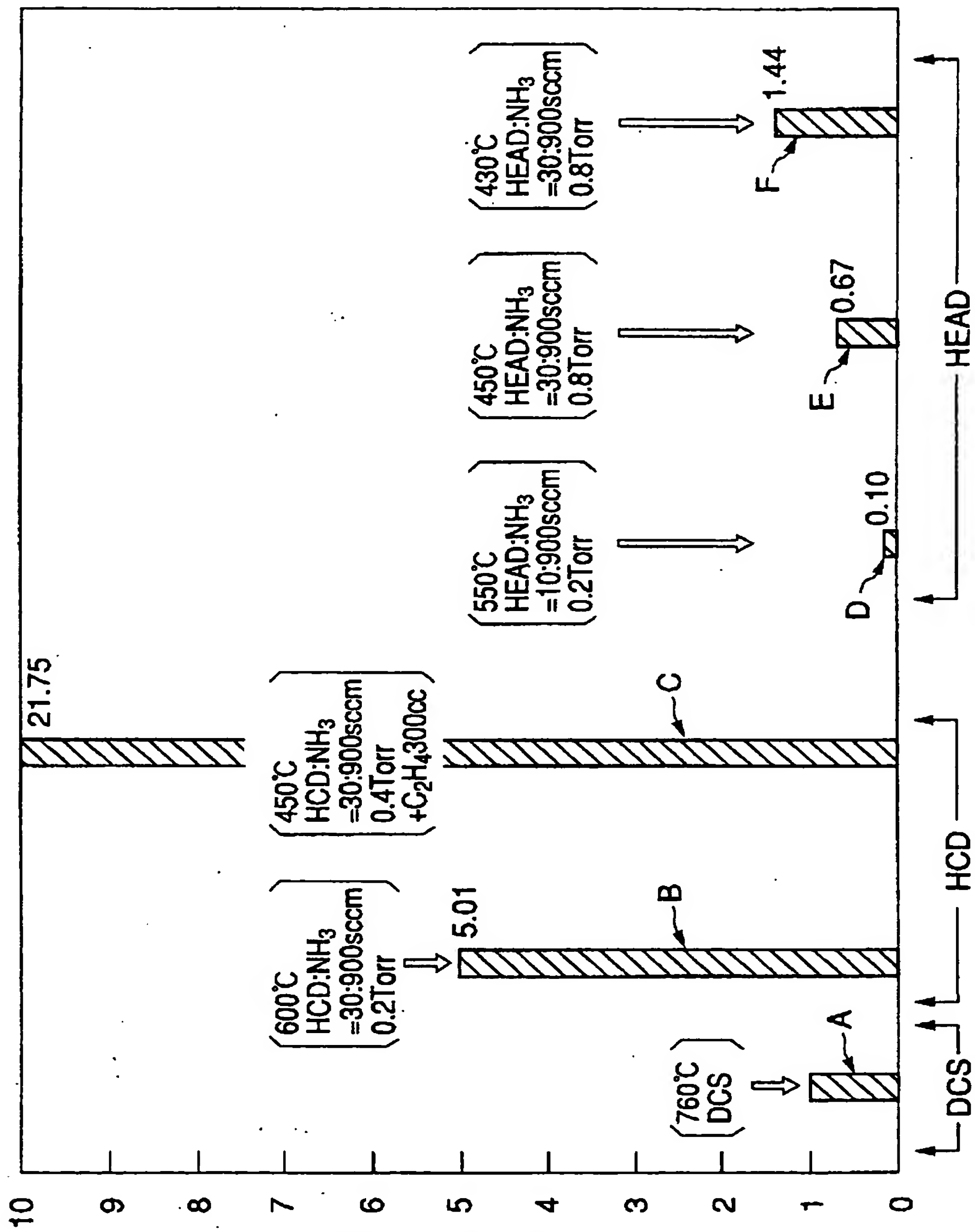
【図1】

FIG. 1


WAFER BOAT (TARGET SUBSTRATE SUPPORTING MEANS)
20 ウエハボート(被処理体支持手段)
16 加熱炉
HEATING COVER
8 処理容器
PROCESS CHAMBER
12 加熱手段
HEATING MEANS
2 成膜装置
FILM-FORMATION APPARATUS
14
4
6
10
12
12
18A
18
26
30
28
S
22
24
W
W
50
48
36
32
34
38
排気
40
ガス供給手段
GAS SUPPLY MEANS
62
60
56
54
EXHAUST PORT
44
42
NH3
HEAD
(ヘキサエチルアミノジシラン)
HEXAETHYLAMINODISILANE

【図2】

FIG. 2



正規化エッチングレート

NORMALIZED ETCHING RATE

[Document] ABSTRACT

[Abstract]

[Object] To provide a film-formation method in which the etching rate of a film during a cleaning process can be made relatively small even if the film is formed at a relatively low temperature. Thus the cleaning process is performed with high controllability in the film thickness.

[Means for Achieving the Object] In a film-formation method of supplying a process gas into a process container 8 which can be evacuated and forming a silicon nitride film on a target substrate at a predetermined process temperature, ammonia gas and hexaethylamino-disilane gas are used as the process gases. This can make the etching rate of a film during a cleaning process relatively small even if the film is formed at a relatively low temperature.

[Elected Figure] FIG. 1